

# REACTIONS OF MODEL COMPOUNDS OF PHENOL RESIN IN SUB- AND SUPER-CRITICAL WATER

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## INTRODUCTION

The critical temperature and pressure of water at supercritical conditions are 647.2K and 22.1 MPa, respectively. The dielectric constant, ion product, and viscosity of the water at the critical point are 6, 10-12(Kw:(mol)<sup>2</sup>), and 0.002, respectively. Under supercritical conditions, water, organic compounds and gases are completely miscible. Furthermore, it is pointed out that the supercritical water is emerging as a medium which could provide the optimum conditions for a variety of chemical reactions among them the destruction of hazardous waste.

In recent years, the amounts of waste plastics increase and it becomes a serious problem because of lack of landfill field. The chemical recycling of waste plastics into their monomers has been gaining greater attention as a means of obtaining valuable products from waste plastics. The plastics are classified into thermoplastic resin and thermosetting resin. In the case of thermoplastic resin such as polyesters and polyamide, chemical recycling process has been reported. However, chemical recycling process for thermosetting resin wastes such as phenol resin waste has not been yet reported. Recently, we have communicated our findings on chemical recycling process for thermosetting resin wastes such as phenol resin waste (1-3). We have been studying on decomposition of polymeric compounds such as cellulose in water at supercritical conditions. In this study to obtain information of the role of water on chemical reaction of phenol resin waste, we have tried the decomposition reaction of model compounds of phenol resin such as p- and o-bis(hydroxyphenyl)methane, and various prepolymers.

## EXPERIMENTAL

Decomposition reaction in water was carried out in 10 ml tubing bomb reactor. The reactants such as p- and o-bis(hydroxyphenyl)methanes were commercially available in a purity of 98% or higher and were used without further purification. 0.1g of model compound and 1 - 4 ml of water were introduced in the reactor. The reaction temperatures were 523 to 703K and reaction times were 0.25 to 1h. Reaction products were extracted by ether. The organic phase was concentrated using an evaporator. It was dissolved with organic solvent after adding a standard. The reaction products were identified by GC/MS and quantified by GC with a flame ionization detector (FID). In the case of GC/MS, the oven temperature was held at 333K for 3 min at initial stage. After then the oven temperature increased from 333K to 493K at a rate of 10K/min. The final temperature was maintained for an additional 6 min. In the case of GC the oven initial temperature was 403K and the oven temperature increased 503K at a rate of 10 K/min. The final temperature was maintained for an additional 6 min. Basic compound such as NH<sub>4</sub>OH, NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub> was added.

## RESULTS AND DISCUSSION

### Decomposition reaction of model compounds in supercritical water

It is well known that thermal cleavage of methylene bond is not easy. However, we have found that methylene bond was cleaved in the reaction of phenol resin model compound with supercritical water. In the reaction of p-bis(hydroxyphenyl)methane, it was decomposed to their monomers such as phenol, p-cresol, o-cresol and 2,4-dimethylphenol. To obtain information on the reaction mechanism of decomposition reaction in water, p-bis(hydroxyphenyl)methane (compound 1), o-bis(hydroxyphenyl)methane (compound 2), diphenylmethane (compound 3), di-p-tolylmethane (compound 4), dibenzyl (compound 5) were reacted at 573 to 703K for 1h. However, model compounds 3, 4 and 5 were scarcely decomposed even by the reaction at 703K for 1 h. Compounds 1 and 2 easily decomposed in the reaction with supercritical water. It was considered that the presence of hydroxyl groups was essential for the decomposition reaction. We have tried to add phenol in the reaction of compound 3, however, no acceleration of decomposition reaction was observed. It indicates that the reactant

itself should possess hydroxyl groups. Model compound 1 decomposed into monomers such as phenol, p-cresol, o-cresol, and 2,4-dimethylphenol at 703K. Also, we have confirmed the productions of benzaldehyde and p-dihydroxybenzene by the reaction at 573K for 0.25h, although the yields of them were small. They were unstable at high temperature and the presence of them were not confirmed by the reactions at over 623K. The results suggested the direct participation of water as a reactant in the decomposition. Model compound 2 decomposed into their monomers such as phenol, p-cresol, o-cresol and so on. The production of xanthene was also confirmed. Phenol and cresol were main products. Xanthene was undesirable dehydrated product of compound 2. Even in the neat reaction at 703K for 0.25h, the yield of xanthene reached 20.2% although the yield of phenol was only 7.4%. Although conversion of compounds 1 and 2 reached more than 70% at 703K for 1h, the yield of identified products was less than 50%, indicating the presence of unidentified products. We confirmed the presence of trimer of phenol by the GC/MS analysis of water soluble products although we could not quantify. It indicated the presence of condensation reactions.

#### The effect of hydrogen donor, tetralin on the decomposition reaction

If the decomposition reaction proceeded via radical intermediates, the addition of hydrogen donor should be effective to avoid the condensation reaction. Therefore, hydrogen donor, tetrahydronaphthalene(tetralin), was added to the reaction of compounds 1 and 2 with water. The addition of tetralin for the decomposition reaction of compound 2 was effective. Although the yields of phenol and xanthene were 10.3% and 18.4% at 703K for 0.5h, they became 32.9% and 2.0% by the addition of tetralin. Xanthene was stable in supercritical water.

The addition of tetralin was effective to prevent the production of xanthene. However, the addition of tetralin was not effective for the decomposition reaction of compound 1. Position of hydroxyl groups was important for the decomposition reaction.

#### The effect of the addition of acid and alkali salt

The addition of hydrogen donor was not effective for the decomposition reaction of compound 1 indicating that radical reaction was not so important. If the ionic decomposition reactions occurred, the addition of acid or alkali salts might be effective to avoid the condensation reaction. The addition of acid was not effective for the reaction of compounds 1 and 2. However, the addition of alkali salts was effective and the yields of reaction products increased on the reactions of compounds 1 and 2. The addition of  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  was more effective than the addition of  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$  or  $\text{K}_2\text{CO}_3$ . In the case of the compound 2, the yields reached more than 60% at 703K for 0.5h and yield of xanthene decreased by the addition of  $\text{Na}_2\text{CO}_3$ . These results indicated that the reaction proceeded via the ionic processes. It was considered that both ionic radical reactions occurred in the decomposition reaction of compound 2. Even by the addition of small amounts of  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ , a total yield of phenol and cresol reached 50% at 673K for 0.25h when additive/model compound ratio was 0.02. For the yields of phenol in the decomposition reactions, 0.1% was the best among these concentrations.

#### The effect of the addition of NaCl

To obtain information on the mechanism of the effects of alkali salt addition, neutral salt, NaCl was added. The yield of phenol in the reaction of compound 1 increased from 7.0% to 11.0% at 703K for 0.25h by the addition of NaCl. It is well known that the addition of NaCl increased the density of water at near supercritical region. The increment of the yield was not large. It indicates that the role of  $\text{Na}_2\text{CO}_3$  was not only to increase water density.

#### The effect of water density

Decomposition reactions were carried out by varying the injection amounts of water from 1 ml, 2 ml to 4 ml. A yield of products increased for the decomposition reactions of compounds 1 and 2 and yield of xanthene decreased with an increase of injection amounts of water. In the reaction in 4 ml of water, a yield of products also increased by the addition of  $\text{Na}_2\text{CO}_3$  although the increment of the yield by the addition was small. The large effect of water on the decomposition reaction indicated that the density was important factor for the decomposition of compounds 1 and 2 in these reaction conditions.

#### Decomposition reaction of prepolymer of phenol resin

Seven prepolymers whose molecular weights were 247-923 were reacted with supercritical water at 703K for 0.5h. Prepolymers were kindly provided by Dainippon Ink & Chemicals Co., Ltd, and their exact compositions were unknown. Main decomposition products from prepolymers A and C were phenol and p-isopropylphenol. It indicated that prepolymers A and C were isopropylphenol resins. Also the main decomposition products from prepolymers F and G were o-cresol, p-cresol and 2,4-dimethylphenol. It indicated that they were cresol resins.

Based on the model compound studies, decomposition reactions of prepolymers were carried out by adding 1wt% Na<sub>2</sub>CO<sub>3</sub> for prepolymer. The yields fairly increased in the case of isopropylphenol resins, prepolymers A and C, and yields of phenol reached 48.9% and 58.0%. The total yields of identified products reached more than 90%. Certainly, reactivities of prepolymers were larger than those of compounds 1 and 2.

## Conclusions

In this study we have clarified that water is excellent solvent for the decomposition reaction of phenol resin containing methylene bridges. The addition of tetralin was effective for the decomposition reaction of bis(o-hydroxyphenyl)methane. The yields of products increased and yield of xanthene decreased by the addition of tetralin. The addition of alkali salts was effective for the decomposition reactions of bis(p-hydroxyphenyl)methane and bis(o-hydroxyphenyl)methane. The significant increment of the yield was observed by the addition. It was suggested that the density was important factor for the decomposition of phenol resin model compounds such as bis(o-hydroxyphenyl)methane and bis(p-hydroxyphenyl)methane in these reaction conditions. Acceleration mechanism of alkali salts addition for the reaction was not clear, however, effective decomposition of model compounds and prepolymers of phenol resin was attained by the reaction with supercritical water, especially in the conditions adding alkali salt.

## REFERENCES

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